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XIII. *An Account of Experiments made by Mr. JOHN M^c NAB, at Albany Fort, Hudson's Bay, relative to the Freezing of Nitrous and Vitriolic Acids. By Henry Cavendish, Esq. F. R. S. and A. S.*

Read February 28, 1788.

FROM the experiments made by Mr. M^c NAB, of which I gave an account in the LXXVIth Volume of the Philosophical Transactions, p. 241. it appeared, that spirit of nitre was subject, not only to what I call the aqueous congelation, namely, that in which it is chiefly, and perhaps entirely, the watery part which freezes, but also to another kind, in which the acid itself freezes, and which I call the spirituous congelation. When its strength is such as not to dissolve so much as $\frac{2}{1000}$ of its weight of marble, or when its strength is less than ,243, as I call it for shortness, it is liable to the aqueous congelation solely; and it is only in greater strengths that the spirituous congelation can take place. This seems to be performed with the least degree of cold when the strength is ,411, in which case the freezing point is at $-1^{\circ}\frac{1}{2}$. When the acid is either stronger or weaker, it requires a greater degree of cold; and in both cases the frozen part seems to approach nearer to the strength of ,411 than the unfrozen part. The freezing points, answering to different degrees of strength, seemed to be as follows.

Strength.

Strength. Freezing point.

Strength.	Freezing point.	
,54	$-31\frac{1}{2}^{\circ}$	} spirituous congelation.
,411	$-1\frac{1}{2}$	
,38	$-45\frac{1}{4}$	
,243	$-44\frac{1}{4}$	} aqueous congelation.
,21	-17	

As some of these properties, however, were deduced from reasoning not sufficiently easy to strike the generality of readers with much conviction, Mr. Mc NAB was desired to try some more experiments to ascertain the truth of it; which he was so good as to undertake, and has executed them with the same care and accuracy as the former.

For this purpose, I sent him some bottles of spirit of nitre of different strengths, and he was desired to expose each of these liquors to the cold till they froze; then to try their temperature by a thermometer; afterwards to keep them in a warm room till the ice was almost melted, and then again expose them to the cold, and, when a considerable part of the acid had frozen, to try the temperature a second time; then to decant the unfrozen part into another bottle, and send both parts back to England, that their strength might be examined.

The intent of this second exposure to the cold was as follows. Spirit of nitre bears, like other liquors, to be cooled greatly below its freezing point without freezing: then the congelation begins suddenly; the liquor is filled with fine spicula of frozen matter, and the ice becomes so loose and porous, that, if the process be continued long enough for a considerable portion of the acid to congeal, scarce any of the fluid part can be decanted: whereas, if it be heated in this state till the frozen part is almost, but not intirely, melted,

and

and be again exposed to the cold, as the liquor is then in contact with the congealed matter, it begins to freeze as soon as it arrives at the freezing point, and the ice becomes much more solid and compact.

The intent of decanting the fluid part, and sending both parts back, that their strength might be determined, was partly to examine the truth of the supposition laid down in my former Paper, that the strength of the frozen part approaches nearer to 411 than that of the unfrozen; but it is also a necessary step towards determining the freezing point answering to a given strength of the acid; for as the frozen part is commonly of a different strength from the unfrozen, the strength of the fluid part, and the cold necessary to make it freeze, is continually altering during the progress of the congelation. In consequence of this, the temperature of the liquor is not that with which the frozen part congealed; but it is that necessary to make the remainder, or the fluid part, begin to freeze, or, in other words, it is the freezing point of the fluid part. This is the reason that a thermometer, placed in spirit of nitre, continually sinks during the progress of congelation; which is contrary to what is observed in pure water, and other fluids in which no separation of parts is produced by freezing.

Moreover, from the above-mentioned experiments of Mr. M^cNAB it appeared, that oil of vitriol, as well as spirit of nitre, is subject to the spirituous congelation; but it seemed uncertain, whether, like the latter, it had any point of easiest freezing, or whether it did not uniformly freeze with less cold as the strength increased. For this reason, some bottles of oil of vitriol, of different strengths, were sent, which he was desired to try in the same manner as the former. This point, indeed, has since been determined by Mr. KEIR, who has
shewn

shewn that oil of vitriol has a strength of easiest freezing; and that at that point a remarkably slight degree of cold is sufficient for its congelation.

The result of Mr. M^c NAB's experiments on the nitrous acid is given in the following table.

N ^o	Decanted part.		Undecanted part.		Strength of the whole mafs.	Strength before sent.	Freezing point by first method.	Freezing point by second method.
	Quantity.	Strength.	Quantity.	Strength.				
6	— —	— —	— —	— —	— —	,561	— 41,6	— —
7	1410	,445	2137	,435	,439	,437	+ *1,7	— 3,8
8	1658	,390	1940	,422	,407	,408	— 3,5	— 4
9	1368	,353	2438	,416	,393	,391	— 4,5	— 11
10	2206	,343	1920	,373	,357	,357	— 12,5	— 13,8
11	3620	,310	602	,381	,320	,320	— 22,5	— 23
12	2155	,276	1494	,293	,283	,280	— 39,1	— 40,3
13	1618	,241	1961	,235	,238	,238	— 34	— 32

The first column contains the numbers by which Mr. M^c NAB has distinguished the different bottles. The second and third columns contain the quantity and strength of the decanted part of the liquor; and the fourth and fifth shew the quantity and strength of the undecanted part of the liquor. The sixth column gives the strength of both parts put together, or the strength of the whole mafs; and the seventh is the strength of the same acid, as it was determined before it was sent to Hudson's Bay. The strengths of the decanted and undecanted parts were found by saturating the liquor returned home with marble; and that of the whole mafs was inferred by computation from the quantity and strength of the decanted and undecanted parts; and as the strength thus inferred never differs from that determined before the liquors were sent to Hudson's Bay by more than $\frac{1}{1000}$ part of the

whole, it is not likely that the strengths of the decanted and undecanted parts here set down should differ from the truth by much more than that quantity.

The eighth column contains the freezing points found in the first method, or the temperature of the liquors after the hasty congelation which took place on exposing them to the cold without any frozen matter in them; and the ninth contains their temperature after the more gradual congelation which took place when they were cooled with some frozen matter in them; and as the unfrozen part of the acid was decanted immediately after the temperature had been observed, it follows, that this column shews the true freezing points of the decanted liquors. In like manner the eighth column shews the freezing points of that part of the liquor which remained fluid in the first manner of trying the experiment; but as the strength of this part was not determined, the precise strengths to which these freezing points correspond are unknown. Thus much, however, is certain, that these points must be below those of the whole mass, and in all probability must be above those of the decanted liquor; as there is great reason to think, that the quantity of frozen matter was always less, and consequently the strength of the fluid part differed less from that of the whole mass, in the first way of trying the experiment than in the second.

Before I draw any conclusions from these experiments, it will be proper to take notice of some particularities which occurred in trying them.

N^o 6. was made to congeal by a freezing mixture of snow and diluted oil of vitriol. By the time the acid was cooled to -42° , icy filaments were formed on the inside of the phial above the acid. Ten minutes after, the acid being cooled one
degree

degree more, the phial was taken out and agitated. This mixed the icy filaments with the acid, and made it freeze, which it seems not to have done before, in consequence of which its temperature rose to $-41^{\circ}\frac{1}{2}$. After having melted the greatest part of these filaments, and again exposed it to the freezing mixture, some snow accidentally fell into the acid, and made an uncertainty in the freezing point, for which reason it is not set down. But as it is evident, that the quantity of congealed matter in the first experiment was excessively small, the strength of the unfrozen part could not differ sensibly from that of the whole mass, and therefore $-41^{\circ}\frac{1}{2}$ is the true freezing point that answers to the strength of 561.

It is remarkable, that N° 8. acquired by congelation a bluish colour, not unlike that which the dephlogisticated nitrous acid, in Mr. M^c NAB's former experiments, acquired by dilution with snow. It is not said, how long the acid retained this colour, but it was intirely gone when the phial arrived in England. I am quite at a loss to account for this phænomenon, and why it happened to this bottle only.

N° 12. when cooled to -17° seemed to contain many icy particles; but as it afterwards bore to be cooled to -48° , without their increasing, we may conclude, that they were not frozen spirit of nitre, but only some heterogeneous matter separated from it. A little of the congealed part of N° 8. dropped into it while at this point, made it freeze, and it rose to -39° .

In all the foregoing acids the ice was heavier than the fluid part, and in consequence subsided to the bottom; a proof that it was the spirituous congelation which had taken place in them: but in N° 13. the frozen part swam at top, which shews, that the congelation was of the aqueous kind.

It may appear remarkable to those who read Mr. Mc NAB's experiments, that these acids bore to be heated so much above their freezing points before the ice intirely dissolved. N° 6. bore to be heated 18 degrees, N° 7. 13 degrees, and N° 12. 17 degrees above their freezing points, before all the congealed acid had disappeared. But as, in order to dissolve this congealed matter, they were brought into a room in all probability a great many degrees warmer than the points to which they were heated, so that the liquors heated fast; and as during the dissolution the ice would subside to the bottom; it is not extraordinary, that the fluid part in the phial might be many degrees warmer than the frozen part, unless the phials were much agitated during the time, which nothing shews them to have been; especially if we consider the great quantity of heat which, in all probability, must be communicated to the frozen acid in order to melt it; and that, perhaps, the frozen acid may receive and part with its heat but slowly. It must be observed, that in N° 6. and 12. the frozen part might very likely be of a considerably different strength, and in consequence its freezing point might be several degrees different from that of the whole mass, so that the temperature to which the fluid was heated, in order to melt the ice, might very likely not differ so much from the freezing point of the ice itself as is here set down. But this could not be the case with N° 7.

It must be observed, that when Mr. Mc NAB wanted to try the temperature of N° 7. after it had frozen in the first manner, the stopper stuck so tight that he was not able to remove it without warming it before the fire. The thermometer was then introduced, and stood several minutes therein at $+1^{\circ}\frac{1}{2}$, or $+2^{\circ}$. As the thermometer remained so long at this point, one

might naturally suppose, that this was the true freezing point of the unfrozen acid. But yet, from what has been just said, it seems not improbable that it may be otherwise, and that the true freezing point may be sensibly lower; for which reason it is marked in the table with an asterisk (*) as doubtful.

It was before said, that the temperatures in the ninth column of the foregoing table, are the freezing points answering to the strengths expressed in the third column, and that $-41^{\circ}\frac{1}{2}$ is the freezing point answering to the strength of ,561; whence the freezing points determined by these experiments, and their respective strengths, are as follows :

Strength.	Freezing point.
,561	$-41,6^{\circ}$
,445	$-3,8$
,390	-4
,353	-11
,343	$-13,8$
,310	-23
,276	$-40,3$

By interpolation from these *data*, according to NEWTON'S method †, it appears, that the strength at which the acid freezes with the least cold is ,418, and that the freezing point answering to that strength is $-2^{\circ}\frac{4}{10}$.

In order to shew more readily the freezing point answering to any given strength, I have computed, by the same method, the following table, in which the strengths increase in arithmetical progression.

† Princip. Math. Lib. III. prop. 40. lem. 5.

Strength.

Strength.	Freezing point.	Difference.
,568	- 45,5	+ 15,4
,538	- 30,1	+ 12
,508	- 18,1	+ 8,7
,478	- 9,4	+ 5,3
,448	- 4,1	+ 1,7
,418	- 2,4	- 1,8
,388	- 4,2	- 5,5
,358	- 9,7	- 8
,328	- 17,7	- 10
,298	- 27,7	

It was before shewn, that the freezing points, found by the first method, ought to be below those of the whole mafs, and must, in all probability, be above those of the decanted liquor. In order to see how this agrees with observation, I computed in the above-mentioned manner the freezing points answering to the strength of the whole mafs, and compared them with the observed freezing points. The result is given in the following table.

N ^o	Strength of the whole mafs.	Strength of the decanted liquor.	Computed freezing point of the whole mafs.	Observed freezing point.	
				In first method.	In second method.
7	,439	,445	- 3,2	+ 1,7	- 3,8
8	,407	,390	- 2,6	- 3,5	- 4,
9	,393	,353	- 3,7	- 4,5	- 11,
10	,357	,343	- 10,	- 12,5	- 13,8
11	,320	,310	- 19,9	- 22,5	- 23,
12	,283	,276	- 35,6	- 39,1	- 40,3

It

It may be observed, that the freezing point of N° 7. tried in the first way, is considerably above that corresponding to the strength of the whole mass; but as this experiment was shewn (in p. 173.) to be doubtful, and not unlikely to exceed the truth, we may safely reject it as erroneous. All the others, as might be expected, are lower than those corresponding to the strength of the whole mass, and above those observed in the second manner, and therefore serve to confirm the truth of the above determination of the freezing points of spirit of nitre; and also shew, that in this acid the point of spirituous congelation is pretty regular, and does not depend much, if at all, on the rapidity with which the congelation is performed.

The point of aqueous congelation, however, seems liable to considerable irregularity; for N° 13. after having been exposed to the cold, froze on agitation, the congelation, as was before said, being of the aqueous kind, and the thermometer stood stationary therein at -34° . The ice being then almost melted, it was again exposed to the cold, till a good deal was frozen; but yet its temperature was then no lower than $-32^{\circ}\frac{1}{4}$, though the quantity of frozen matter must certainly have been much more than in the first trial. The fluid part being then decanted, and the frozen part melted, both were again exposed to the cold. They both were made to congeal by agitation, and the temperature of the undecanted was then found to be -35° , and that of the decanted part -37° : so that it should seem as if the freezing point found by the hasty congelation was always lower than that found the other way, which may, perhaps, proceed from this cause; namely, that when sufficient time is allowed, the watery part will separate from the rest, and freeze in a degree of cold much less than what is required.

required to produce that effect, when it is performed in a more rapid manner.

These experiments confirm the truth of the conclusions I drew from Mr. M^c NAB's former experiments; for, first, there is a certain degree of strength at which spirit of nitre freezes with a less degree of cold than when it is either stronger or weaker; and when spirit of nitre, of a different strength from that, is made to congeal, the frozen part approaches nearer to the foregoing degree of strength than the unfrozen. Likewise this strength, as well as the freezing point corresponding thereto, and the freezing point answering to the strength of ,54, come out very nearly the same as I concluded from those experiments; for by the present experiments they come out ,418, $-2^{\circ}\frac{4}{10}$, and -31° , and by the former ,411, $-1^{\circ}\frac{1}{2}$, and -31° . But the freezing point answering to the strength of ,38 is totally different from what I there supposed. This must have been owing to the strength of that acid having been very different from what I thought it; which is not improbable, as its strength was inferred only from the quantity of snow which was added to it in finding the degree of cold produced by its mixture with snow.

After the foregoing experiments were finished, Mr. M^c NAB made some more for determining the freezing points both of the decanted and undecanted part; but for want of a sufficient explanation of the manner in which they were executed, I have not been able to make any use of them. In their present state they shew much appearance of irregularity; but this would very likely have been cleared up, if the circumstances had been more fully detailed.

On the Vitriolic Acid.

An irregularity of a remarkable kind occurred in trying two of these acids; namely, when the undecanted part was melted and again made to congeal, its freezing point was found to be much less cold than that of the decanted part, and the difference was much greater than could be attributed to the difference of strength. This seems to have happened only in the two strongest acids, namely, N^o 1. and 2. and in great measure confirms the supposition which I formed from Mr. Mc NAB's former experiments, that the congealed part of oil of vitriol differs from the rest, not merely in strength, but also in some other respect, which I am not acquainted with. It should seem, however, that this property does not extend to weak oil of vitriol.

It perhaps may be suspected, that this property takes place in the nitrous acid also, and was the cause of the slow melting of the ice taken notice of in p. 172. But I think it more likely, that that phenomenon proceeded from the causes there assigned.

Some smaller irregularities occurred in trying the vitriolic acid, the cause of which I believe was, that when this acid has been cooled below the freezing point, and begins to freeze, the congelation proceeds but slowly; so that a considerable time elapses before it rises to the true freezing point. Something of the same kind seems to take place in the nitrous acid also, though in a less degree; for the decanted liquors usually continued to freeze and deposit a small quantity of ice, for a few minutes after they were poured off, though their cold, at least in some instances, was found rather to diminish during that time.

It must be observed, that small spicula of ice always came over along with the decanted liquor; and to this, in all probability, the new-formed ice attached itself; for otherwise it is likely, that no ice would have been produced.

The following table contains the strength of the acids as determined before they were sent to Hudson's Bay, and the quantity and strength of the decanted and undecanted parts when they arrived at London, and the strength of the whole mass as computed from thence. For the sake of uniformity, I have expressed their strengths, like those of the nitrous acid, by the quantity of marble necessary to saturate them, though I did not find their strength by actually trying how much marble they would dissolve; as that method is too uncertain, on account of the selenite formed in the operation, and which in good measure defends the marble from the action of the acid. The method I used was, to find the weight of the plumbum vitriolatum formed by the addition of sugar of lead, and from thence to compute the strength, on the supposition that a quantity of oil of vitriol, sufficient to produce 100 parts of plumbum vitriolatum, will dissolve 33 of marble; as I found by experiment that so much oil of vitriol would saturate as much fixed alkali as a quantity of nitrous acid sufficient to dissolve 33 of marble. It may be observed, that the quantity of alkali, necessary to saturate a given quantity of acid, can hardly be determined with much accuracy, for which reason the foregoing less direct method was adopted; especially as the precipitation of plumbum vitriolatum shews the proportional strengths, which is the thing principally wanted, with as great accuracy as any method I know.

N ^o	Strength before sent.	Decanted part.		Undecanted part.		Strength of whole mass.
		Quantity.	Strength.	Quantity.	Strength.	
1	,977	1375	,967	3460	,963	,964
2	,918	3915	,919	1876	,905	,914
3	,846	88	,777	4915	,850	,849
4	,758	389	,710	{ 3795 547	{ ,753 ,803	,755

The undecanted part of N^o 4. was divided into two parts; namely, the less and the more congelable part; and it is the latter whose quantity and strength is given in the last line.

It is well known, that oil of vitriol attracts moisture with great avidity; and some of these acids were much exposed to the air during the experiments made with them, and may therefore be supposed to have attracted so much moisture from the air, as might sensibly diminish their strength; and this seems actually to have been the case with some of them. But as the bottles were well stopped, and as, except in one acid which was the most exposed to the air, the strength of the whole mass comes out not much less than that determined before the liquors were sent to Hudson's Bay, I imagine their strength could not sensibly alter during their voyage home; and consequently their strength, at the time the last observations were made with them, could not differ much from that here set down.

It would be tedious to give the experiments for determining their freezing points in detail; but the result is as follows. The freezing point of N^o 1. tried in the first method, was somewhat above + 1°, but it is uncertain how much; that tried in the second manner seemed - 6°½. But the freezing point of the undecanted part, after having been intirely melted, and again

exposed to the cold, was $+9^{\circ}$. It must be observed, that though this part was in all probability at first stronger than the decanted part, yet at the time its freezing point was tried, it seems to have become rather weaker than that, owing to its exposure to the air. It was before said, that the freezing point tried in the second manner is that of the decanted liquor; so that the freezing point of the decanted part seems to have been 13 or 14 degrees colder than that of the undecanted part; though the difference of strength, if there was any, must in all probability have tended to produce the contrary effect.

The freezing point of N^o 2, tried in the first way, was $+26^{\circ}$; and that tried in the second was -30° , or 26° ; but yet the freezing point of the undecanted part was 26 or 30 degrees higher, namely, at zero; a difference which could scarcely have proceeded from the difference of strength.

The freezing point of N^o 3, could hardly differ much from $+42^{\circ}$; and that of N^o 4, was about -45° .

It should be remarked, that when this last acid, as well as N^o 1. and 2. were exposed to a great cold, a sediment formed in them. This must have been of a very different nature from frozen acid, as appeared both from its texture, which was soft and mucilaginous to the feel, instead of being gritty as the frozen acid always was; and also from its being not much increased by an increase of cold; and therefore seems to have been some impurity separated from the acid. The quantity was greatest in N^o 4.; but even in this, though it appeared great, it is likely that the real quantity was very small.

Another bottle of acid, whose strength was .659, was sent; but Mr. M^c NAB was not able to make this freeze.

From these experiments it should seem, that the freezing point

point of oil of vitriol, answering to different strengths, is, nearly as follows :

Strength.	Freezing point.
,977	+ 1°
,918	- 26
,846	+ 42
,758	- 45

From hence we may conclude, that oil of vitriol has not only a strength of easiest freezing, as Mr. KEIR has shewn ; but that, at a strength superior to this, it has another point of contrary flexure, beyond which, if the strength be increased, the cold necessary to freeze it again begins to diminish.

The strength answering to this latter point of contrary flexure must, in all probability, be rather more than ,918, as the decanted or unfrozen part of N° 2. seemed rather stronger than the undecanted part ; and for a like reason the strength of easiest freezing is rather more than ,846.

Mr. KEIR found that oil of vitriol froze, with the least degree of cold, when its specific gravity at 60° of heat was 1,780, and that the freezing point answering to that degree of strength was + 46° ; which agrees pretty nearly with these experiments ; as the strength of oil of vitriol of that specific gravity is ,848, that is, nearly the same as that of N° 3.



